Renewable Thermoset Copolymers from Tung Oil and Natural Terpenes

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ABSTRACT: The cationic copolymerization of tung oil, limonene, and myrcene as comonomers, initiated by boron trifluoride, is presented and discussed in this work. Dynamic mechanical analysis revealed that all copolymers behave as thermosets. FTIR spectra for both copolymers, after extraction with dichloromethane, suggested that the major component of the insoluble fraction was reacted tung oil (a cross-linked triglyceride network). Likewise, unreacted tung oil was found to be the main component of the soluble phase. Also, all the copolymers showed only one tan δ peak, indicating no phase separation. Glass transition temperature (Tg) increased with the myrcene content and decreased almost linearly as the limonene content increased. Furthermore, the Fox and Loshaek model showed a relatively good prediction of the Tg values of the polymers. The Young's modulus ranged from 33.8 to 4.7 MPa for all tested thermosets. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41155.

INTRODUCTION

The search for sustainable chemistry has led to the development of new synthetic routes to produce polymers from renewable resources. Lately, particular attention has been paid to biomass as a source of a wide range of biomaterials. Amongst many biomass derived materials, it is important to highlight the potential use of vegetable oils. The employment of these materials as platform chemical for polymer synthesis has several advantages, which include availability, inherent biodegradability, high purity, and low toxicity.[1] Vegetable oils or triglycerides are fatty acid esters of the triol glycerol. Most of them contain fatty acids with chain lengths within the range of C_{16} to C_{22}, with C_{18} fatty acids dominating. Basically, a fatty acid consists of a hydrophobic hydrocarbon chain with a hydrophilic group at one end. The degree of unsaturation varies according to the composition of fatty acids presenting double bonds. This value, one of the most important parameters in the chemistry of fatty acids and triglycerides, can be calculated through the iodine value, a structural index which has been related to various physical and chemical properties and has served as a quality control method in hydrogenation reactions.[2]

Likewise, besides the carbon–carbon double bonds, some plant oils exhibit fatty acids containing other functional groups such as hydroxyls, cyclic groups, epoxy groups, etc. which are amenable for developing chemical reactions and structural modifications. According to the literature, there are three main routes for the synthesis of polymers from plant oils. The first approach corresponds to the direct polymerization through the C=C bonds.[3,4] Their presence allows the polymerization of the oils into solid polymeric materials either through free radical or cationic mechanisms.[5–7] The second route consists of the functionalization of the double bonds to insert more reactive groups, usually epoxy, amine, or hydroxyl, etc.[8,9] They can be considered as an intermediate product for subsequent reactions to yield bio-based polymers such as polyurethane, polyester, etc. The third approach focuses on the chemical transformation of vegetable oils to produce platform chemical which can be used to produce monomers for the polymer synthesis.[10]

Regarding the direct polymerization of the C=C, the free radical polymerization has received little attention because of the presence of many side reactions. On the other hand, the cationic polymerization has been studied by several researchers with successful results.[11,12] The cationic copolymerization reaction usually requires an initiator. Several Lewis acids, such as $AlCl_3$, $TiCl_4$, $SnCl_4$, and BF_3-OEt_2 (BFE) amongst others, have been used as initiators to copolymerize vinyl monomers cationically under relatively mild reaction conditions. As reported by some researchers,[13,14] BFE has proved to be a very efficient initiator in cationic polymerization of vegetable oils. Usually, a trace of water or a diol, acting as a co-initiator is needed to protonate the monomer. Triglycerides in general are cationically polymerizable monomers. The accepted mechanism for such polymerizations is similar to that proposed for cationic polymerization of vinyl monomers.[15] Each unsaturated fatty acid chain can participate in the reaction, and the presence of several

unsaturations leads to an extensive cross-linking. Tung oil (TO), containing a conjugated triene, is very reactive and highly susceptible to polymerization via a cationic mechanism, because the intermediate carbocation can be stabilized by resonance.[1] Likewise, vegetable oils can be polymerized with reactive monomers in order to vary the properties of the oil-based matrix.[13] Because of the presence of multiple functional sites per triglyceride molecule, which allow them to cross-link, oils can be considered as analogous to vinyl esters and unsaturated polyesters.[17]

Terpenes, natural monomers having carbon skeletons of isoprene units, are found in many essential oils and represent a versatile chemical feedstock.[18] Even though the use of terpenes in chemical synthesis is vast and well supported by a large number of publications, their applications in polymer science are scarce and far between, usually limited to attempts to polymerize bicyclic monoterpenes, such as α and β pinene by Lewis acid and Ziegler-Natta catalysis.[19,20] As stated by Norström,[21] terpenes do not tend to polymerize, and their lack of reactivity can be attributed to both steric hindrance and low stabilization energy between the monomer and the chemical species in the transition state. However, as terpenes exhibit carbon–carbon double bonds amenable to reactions, several works have been published concerning the polymerization of terpenes with vinyl monomers in order to develop biodegradable polymeric materials.[22–24]

Envisioning the oil molecules as chains bearing multiple vinyl monomers, the main purpose of this project is to cover the major aspects related to the synthesis, characterization as well as properties of new macromolecular bio-based thermoset polymers, produced through the cationic copolymerization of tung (a natural oil) with three different terpenes; such as limonene (Lim), myrcene (Myr), and linalool (Lin) as reactive comonomers. Also, in order to compare the properties of the resulting materials, TO was copolymerized with styrene, a widely studied synthetic monomer. The chemical, physical, and mechanical properties of these new polymeric materials were investigated as a function of the proportion and type of reactive monomer included in the mixture.

METHODS

Materials
TO, Lim, Myr, and Lin were purchased from VWR International (US) and used with no further purification. Styrene (ST) was purchased from Aldrich Chemical Company (US) and used as received. Tetrahydrofurane (THF) was used as an initiator modifier and was supplied by VWR International (US). Boron Trifluoride Etherate (BFE) was employed as an initiator and 1,4-butanediol was used as co-initiator; both were acquired from VWR International (US).

Polymer Preparation Via Cationic Polymerization
The polymeric materials were prepared by cationic polymerization initiated by modified BFE. The desired amount of the comonomer was measured out and added to the TO. The mixture was vigorously stirred followed by the addition, drop by drop, of the appropriate amount of the modified initiator. The

modified catalyst was prepared by dissolving the boron trifluoride diethyl etherate and 1,4-butanediol in the desired amount of THF. The reaction mixture was placed into an aluminum mold and heated for a given time, usually 12 h at room temperature, followed by 12 h at 60°C and finally for 12 h at 110°C.

Characterization
Soxhlet extraction was employed to characterize the structures of the bulk copolymers. An appropriate amount of the bulk polymer was extracted for 24 h with 200 mL of refluxing dichloromethane with a Soxhlet extractor. Upon extraction, the resulting solution was concentrated by rotary evaporation and subsequent vacuum drying. The soluble substances were isolated for further characterization. The insoluble solid was dried in a vacuum oven for several hours before it was weighed. FTIR spectra of both the soluble and insoluble fraction extracted by Soxhlet were recorded. The densities of the copolymers were determined by pycnometry.

Mechanical properties of the resulting polymers were obtained by dynamic mechanical analysis (DMA). To be able to explain the effects of the co-monomers on the mechanical properties, it is useful to calculate the cross-linking density (n, mol/m^3). The crossl-inking density can be estimated from the experimental data using the rubber elasticity theory. Thermosets behave as rubbers above Tg. At small deformations, rubber elasticity predicts that the modulus storage (E'), of an ideal elastomer with a network structure is proportional to the cross-linking density according to the following equation:

$$E' = 3nRT = 3RT\rho/Mc \tag{1}$$

where E' is the rubbery storage modulus, R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), ρ is the density of the sample (g/m^3), and M_c is the molecular weight between cross-links (g/mol). The temperature and rubbery modulus were determined for the calculation of the equation at Tg + 25°C. The temperature at which the peak of the tan delta presents a maximum was considered the glass transition temperature of the material. In order to predict the Tg based on the cross-linking density, the Fox and Loshaek model (which assumes specific volume of the polymer at the glass transition as a linear function of Tg) was employed to study the TO-based copolymers. The Fox and Loshaek expression is shown in the following equation:

$$Tg = Tg^u + K/Mc \tag{2}$$

where K is a material constant, Tg^u corresponds to the Tg predicted by the Fox equation, and M_c corresponds to the molecular weight between cross-linking. The parameter $K = 5.2 \times 10^3$ K g/mol was used to fit the model to the experimental results[17].

RESULTS AND DISCUSSION

Cationic Polymerization of Vegetable Oils
Early in this research, several attempts to develop oil-based materials by cationic polymerization; employing different types of vegetable oils, such as linseed oil, TO, soybean oil, corn oil, etc. were carried out. Keeping in mind the preparation of completely bio-based polymers as the major goal, the triglycerides were copolymerized with terpenes, natural monomers
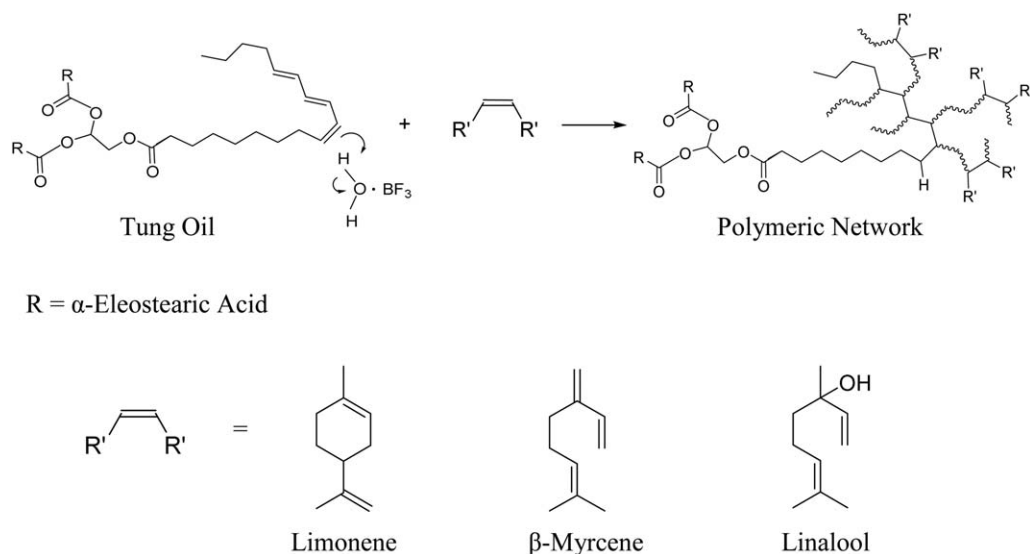
Figure 1. Cationic polymerization of TO with Lim, Myr, and Lin as comonomers using BFE as initiator.

containing alkenyl functional groups amenable to react. Fruitful reactions leading to useful materials were achieved when TO, whose major component is a fatty acid containing three conjugated unsaturations, was copolymerized with Lim and Myr as reactive comonomers (Figure 1).

As pointed by Liu and Erham,[12] the polymerization of 1,2 disubstituted ethylenes containing small side groups easily occurs. Nevertheless, when bulky groups are attached to the double bonds, the polymerization either does not occur or leads to low molecular weight products after long reaction times. The steric hindrance plays a preponderant role during the propagation of the growing chains. It introduces a high energy barrier between the monomer and the growing species, allowing a very limited amount of polymer to be produced. As fatty acids are 1,2 disubstituted ethylene monomers bearing bulky groups, their polymerization is considered energetically unfavorable.

Unlike the other tested oils, TO was found to be highly reactive towards cationic and free radical polymerizations. Its particular reactivity can be associated to its capacity to stabilize, by resonance, the intermediate carbocation generated on the propagation step of the cationic mechanism. In regards to the use of terpenes as comonomers, successful polymerizations were carried out when using Lim and Myr. The polymerization of TO with Lin led to highly porous materials. The gassing generated during curing could be attributed to side reactions between the Lin and the boron trifluoride ethereate. All the copolymers appeared as dark-brown rubbery materials at room temperature. For all the studied comonomers, suitable materials for analysis were not obtained for terpene proportions above 60 wt %.

Characterization of the Polymer Networks
Once the reacting system has reached the gel point, the polymeric matrix is composed of two fractions, the insoluble gel fraction and the soluble sol fraction. In order to characterize both fractions, samples containing 80 wt % of TO (20 wt % comonomer) were Soxhlet extracted using dichloromethane as a refluxing solvent. The study of the two phases, as well as the

pure TO (to track any possible change in its structure during curing) was developed through FTIR spectroscopy.

The TO structure was characterized by the presence of a conjugated triene, which showed IR absorption bands at 3010, 990, and 960 cm^{-1}. The ester carbonyl exhibited two strong peaks at 1750 and 1150 cm^{-1}. Methylene and methyl groups showed absorption bands at 2925 and 2854 cm^{-1}, as well as at 1465 and 1370 cm^{-1}. An inspection of the FTIR spectrum of the insoluble fraction revealed that the major component in this phase was reacted oil (a cross-linked triglyceride network). The spectrum presented similar absorption bands to those exhibited by the TO. The most remarkable difference between them was the disappearance of the weak peak at 3010 cm^{-1} (attributed to the presence of unsaturations in the TO structure). The lack of this absorption peak in the FTIR spectrum of the insoluble fraction could be related to the fact that the majority of double bonds had been consumed during the polymerization, either to react with other fatty acid chains or with the comonomer, leading to the disruption of the conjugated triene, responsible for the high reactivity of this oil. Upon extraction, for copolymers 80 wt % TO-20 wt % comonomer, around 81–84 wt % of insoluble materials were retained. For all the remaining copolymers, the retained insoluble materials ranged from 76 to 85 wt % after Soxhlet extraction. FTIR analysis of the soluble fraction of the copolymer 80 wt % TO-20 wt % comonomer suggested that the main component presented in this phase was unreacted oil.

Thermo-Mechanical Behavior
DMA measurements are intensively used to investigate the amorphous phase transitions of polymers as they are stressed under periodic deformation. DMA can be used to obtain the storage modulus and the loss modulus as a function of temperature at a given frequency. Figure 2 shows the temperature dependence of the storage modulus for the copolymers TO–Lim. Results revealed that the materials behaved as thermosets. As seen in the curves, the storage modulus initially remained approximately constant. As the temperature increased, the storage modulus
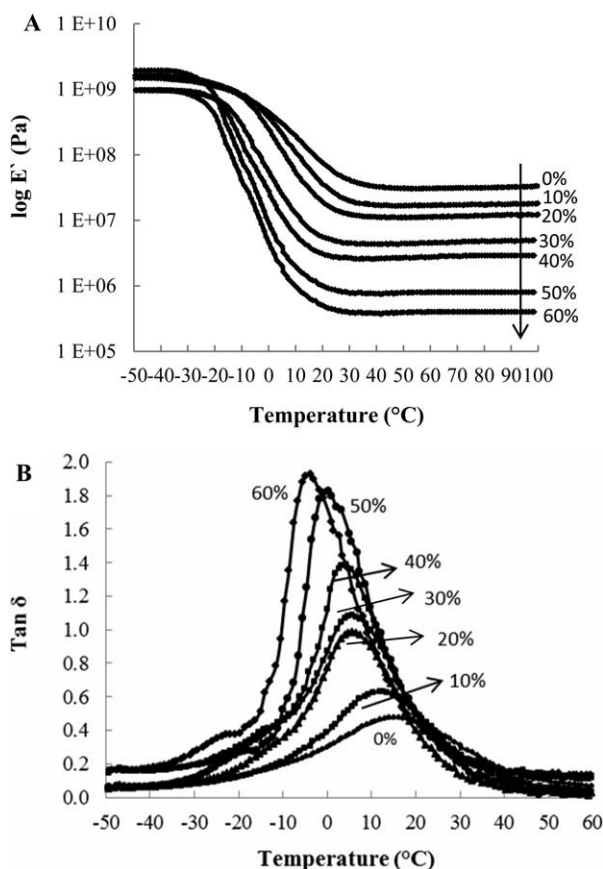
Figure 2. Temperature dependence of the (A) storage modulus (E') for the copolymers TO–Lim and (B) loss factor (tan δ) as a function of the temperature for the TO–Lim copolymers.

exhibited a drop over a wide temperature range (glass transition), followed by a modulus plateau at high temperatures, where the material behaved like a rubber. This region, called the rubbery plateau, evidences the presence of a stable cross-linked network. The modulus drop is associated with the beginning of segmental mobility in the cross-linked polymer network; whereas the constant modulus at temperatures above 30°C is the result of the cross-linked structure of the copolymer.[7] The same behavior has been reported by Li and Larock.[25]

The curves of the loss factor (tan δ) as a function of the temperature for the TO–Lim copolymers are shown in Figure 2. The peak in tan δ corresponded to the main mechanical relaxation of the matrix, which can be used as a criterion to determine the Tg of the copolymer. As can be seen, the transition between the glassy to the rubbery state was wide and began below room temperature for all the tested materials. Likewise, all the copolymers showed only one tan δ peak, indicating that there was no phase separation. The results showed that the peaks shifted to lower temperatures (indicating a decrease in the glass transition temperature), increased in height and become narrower when increasing the co-monomer weight proportion. The peak width at half height is a criterion used to indicate the homogeneity of the amorphous phase. A higher value implies higher inhomogeneity of the amorphous phase. In this particular case, the narrowing and increase in height of the loss factor peaks could be associated to less cross-linked and heterogeneous networks with narrower molecular weight distribution of the chains between cross-linking points.[7] Table I summarizes the properties of the TO–Lim copolymers. As shown, the storage modulus, the cross-linking density and Young's modulus decreased when the TO concentration increased. On the other hand, Tg decreased almost linearly with the increase in the Lim content. Pycnometry showed variations in the density of the copolymers for percentages of Lim higher than 30 wt %.

Fatty acid chains can contribute to two different effects, either plasticizing the network because of the more flexible structure or increasing the rigidity because of the large number of unsaturations per molecule.[26] Both factors can contribute to the properties of the copolymers. In the case of TO–Lim materials, a decrease in both the number of cross-linking points and the glass transition temperature of the networks was observed. As demonstrated by Norstrom,[21] Lim does not tend to homopolymerize (under the experimental conditions reported in Norstrom's work, polymerizing Lim units through cationic polymerization mainly yielded to oligomers that consisted of trimers and tetramers). However, even though it is been clearly stated that formation of large molecules (homopolymerization) out of this terpene not likely to occur, several works have proved that Lim is able to react with vinyl monomers leading to copolymers in which terpene units have been incorporated into the vinyl resin. Because of the inability of Lim to form long chains (even at high weight proportions), here it is suggested that the decrease in the number of cross-linking points arises as a result of Lim units that have been incorporated into the fatty acid chains, lowering their ability to form an oil-based cross-linked network. The decrease in the glass transition of the

Table I. Properties of the Tung Oil–Limonene Copolymers

Limonene proportion (wt %)	Storage modulus (MPa)	Tg (°C)	Cross-linking density, n (mol/m^3)	Density (g/cm^3)	Young's modulus (MPa)
0	32.5	18.28	4117.89	1.0036 ± 0.0027	33.8 ± 2.92
10	17.8	13.89	2287.06	1.0097 ± 0.0020	14.95 ± 1.90
20	11.4	10.53	1480.69	1.0068 ± 0.0132	10.40 ± 0.26
30	4.5	5.58	594.01	1.0080 ± 0.0252	6.34 ± 1.62
40	2.7	4.33	356.55	0.9839 ± 0.0036	3.38 ± 0.31
50	0.83	0.17	111.82	0.9764 ± 0.0151	3.26 ± 0.07
60	0.48	−3.83	64.71	0.9414 ± 0.0081	2.22 ± 0.12

Table II. Properties of the Tung Oil–Myrcene Copolymers

Myrcene proportion (wt %)	Storage modulus (MPa)	Tg (°C)	Cross-linking density, n (mol/m^3)	Density (g/cm^3)	Young's modulus (MPa)
0	32.5	18.28	4117.89	1.0136 ± 0.0057	33.80 ± 2.92
10	22.5	12.38	2905.01	1.0097 ± 0.0028	9.59 ± 1.72
20	14.6	15.31	1867.41	1.0098 ± 0.0082	5.36 ± 0.44
30	7.29	17.71	925.34	1.0102 ± 0.0152	3.22 ± 0.15
40	3.36	22.32	420.36	1.0134 ± 0.0360	1.31 ± 0.06
50	1.26	25.44	156.11	1.0092 ± 0.0101	0.59 ± 0.01
60	0.269	29.82	32.88	1.0109 ± 0.0181	0.21 ± 0.03

networks at high Lim contents, in which cross-linking is very low, is driven by the glass transition of the Lim oligomers (small linear segments) formed during heating of the polymeric matrices.

DMA of the TO–Myr copolymers revealed a similar behavior to that shown by the TO–Lim copolymers. When the temperature increased, the storage modulus exhibited a drop over a wide temperature range, followed by a modulus plateau at high temperatures, evidencing the presence of a stable cross-linked network. Also, the modulus decreased as the Myr proportion in the mixtures increased. The transition between the glassy to the rubbery state for these copolymers was wide and began below room temperature. Likewise, for all the copolymers, no phase separation was observed. The results showed that the tan δ peak increased in height and become narrower as the Myr content in the matrix increased. As in the case of TO–Lim copolymers, this phenomenon could be attributed to the presence of less heterogeneous networks. Unlike the TO–Lim materials, the maximum in the loss factor shifted to higher temperatures when increasing the Myr proportion above 10 wt %, indicating that the glass transition temperature for these copolymers increased as the comonomer proportion increased. Table II summarizes some of the properties of the TO–Myr copolymers. As shown, the glass transition temperature increased with the content of Myr for percentages higher than 10 wt %. Likewise, the increase in the comonomer proportion decreased the amount of cross-linking points in the copolymers. The storage modulus, along with Young's modulus, decreased with the content of Myr. The pycnometry test did not show appreciable changes in the density with the change in the monomer proportion.

Myr is a natural conjugated diene that has been researched as a monomer for the preparation of 100 wt % biosource elastomeric materials. Polymyrcene has been prepared by several methods, including anionic polymerization with *sec*-BuLi and more recently, was homopolymerized by a free radical process in aqueous media.[27] Myr yields polymers with different structures, as a result of the three possible electrophilic additions to the conjugated diene placed in the molecule; being the 1,4 addition the predominant one (77–85%) and 3,4 addition in lesser degree (15–23%).[28] Unlike other common 1,3-dienes (such as butadiene or isoprene), Myr provides polymers with structural units bearing an additional double bond in its alkyl tail, which is very suitable for cross-linking.

When polymerizing Myr and TO in the presence of BFE, the Myr, contrarily to the Lim, is not only able to react with the oil, but it is also capable of homopolymerizing and creating linear Myr–Myr sequences. When increasing the amount of comonomer, the diluting effect of the Myr sequences immersed into the resin becomes predominant, and hence, the cross-linking density decreases, consequently leading to a decrease in the storage modulus. The increase in the glass transition of the networks when increasing the Myr content is attributed to the presence of these linear Myr–Myr sequences formed during heating. As mentioned above, these linear polymyrcene sequences contain structural repeating units bearing very short dangling chains having an extra double bond, which can be prompt to react under the experimental conditions. At high Myr concentrations, these additional unsaturations can react and generate polymyrcene cross-linked networks. The bonding of these polymyrcene linear segments (embedded in the matrix) through crosslinking, stiffs and strengths the system and therefore; limits the segmental motion of the polymer chains, driving the glass transition temperature to higher values whilst increasing the terpene content.

In order to compare the results obtained in this research with previous works dealing with copolymerization of vegetable oils and synthetic vinyl monomers, TO was copolymerized with styrene in the presence of boron trifluoride as an initiator, at room temperature. Table III summarizes the properties of the TO – styrene copolymers. The glass transition temperatures (Tg) increased almost linearly with the content of styrene for percentages higher than 10 wt %. The increase in TO concentration increased the amount of cross-linking points in the copolymers. The storage modulus, along with Young's modulus, decreased with the content of styrene. The pycnometry test also did not show any appreciable change in the density with the variation in the monomer proportion.

Just like in the cases of TO–Lim and TO–Myr, the modulus was found to be strongly dependent on the comonomer proportion. It exhibited a drop over a wide temperature range, followed by a modulus plateau at high temperatures, evidencing the presence of a stable cross-linked network. All the copolymers showed only one tan δ peak denoting, like in the other cases, the homogeneity of the materials. The height of the tan δ peak increased as the styrene content in the matrix increased. The maximum in the loss factor shifted to higher temperatures

Table III. Properties of the Tung Oil–Styrene Copolymers

Styrene proportion (wt %)	Storage modulus (MPa)	Tg (°C)	Cross-linking density, n (mol/m^3)	Density (g/cm^3)	Young's modulus (MPa)
0	32.5	18.28	4117.89	1.0136 ± 0.0057	33.80 ± 2.92
10	14.7	10.00	1912.6	1.0129 ± 0.0087	17.10 ± 2.07
20	10.7	12.04	1383.0	1.0158 ± 0.0033	10.17 ± 0.76
30	8.7	15.91	1109.4	1.0205 ± 0.0121	8.98 ± 0.35
40	6.8	20.15	857.8	1.0238 ± 0.0028	7.30 ± 0.67
50	4.7	27.32	583.9	1.0292 ± 0.0156	6.29 ± 0.23
60	2.9	30.47	353.8	0.9653 ± 0.0178	5.38 ± 0.39

when increasing the comonomer weight proportion, denoting an increment in the glass transition temperature. As Myr, the styrene is not only able to react with the oil, but also, it is capable of homopolymerizing and generating linear styrene–styrene sequences incorporated between the oil matrixes. As increasing the amount of comonomer, the diluting effect of these linear segments immersed into the resin became predominant; leading to a decrease in the cross-linking density (consequently conducing to a reduction in the storage modulus). The increase in the

Figure 3. (A) Glass transition temperature of TO–Lim copolymers as a function of the composition: (▲) values measured with DMA, (◆) linear copolymer contribution, (■) glass transition temperature of the copolymer. (B) Glass transition temperature of TO–mycene copolymers as a function of the composition: (▲) values measured with DMA, (◆) linear copolymer contribution, (■) glass transition temperature of the copolymer.

Tg is also attributed to the presence of these stiff and strong linear Polystyrene segments embedded in the resins.

Theoretical Prediction of Tg Based on the Fox-Loshaek Model
In order to predict the Tg of the copolymers, the Fox–Loshaek model (which assumes specific volume of the polymer at the glass transition as a linear function of Tg) was considered. The model can be considered as the sum of two contributions; the linear contribution Tg^u, predicted by the Fox equation, where the system is assumed to be formed by hypothetical linear molecules; and the cross-linking contribution K/M_c, calculated through the Nielsen equation, which takes into account the cross-linking of those hypothetical linear molecules.[29]

To apply the model, the relation between the Tg and the cross-linking density was studied. Through a simple mathematical approach, the evolution of the glass transition temperature of the copolymers was found to be linearly dependent of the cross-linking density. Thus, employing both the Fox and Nielsen equations, the two contributions for different compositions were calculated. Figure 3 shows the experimental values of the Tg measured by DMA as a function of the Lim content, the linear contribution (Fox equation) and the Tg predicted by the model. As seen, the model was able to predict the general trend in which the Tg decreased as a function of the comonomer content. For the TO polymer (0% Lim) the model overestimated the cross-linking density. For comonomer contents above 40 wt %, the model underestimated the value of the cross-linking density. As previously mentioned, the decrease in the Tg of the networks, at high Lim contents (in which cross-linking lowers), is dictated by the low glass transition of the Lim oligomers. For proportions above 40 wt %, the effect of these oligomers in the system becomes predominant; and the trend in the evolution of the glass transition is driven towards low values.

The same approach was employed to study the evolution of the Tg as a function of comonomer content for the TO–Myr copolymers. As shown in Figure 3, the experimental data closely fit the values predicted by the Fox equation. Even though the model predicted the general trend for the variation in the glass transition temperature, is it important to denote that at high concentrations of Myr, it is capable to form linear molecules, and because of the presence of an additional double bond, it is also able to generate cross-linked Polymyrcene molecules. Under
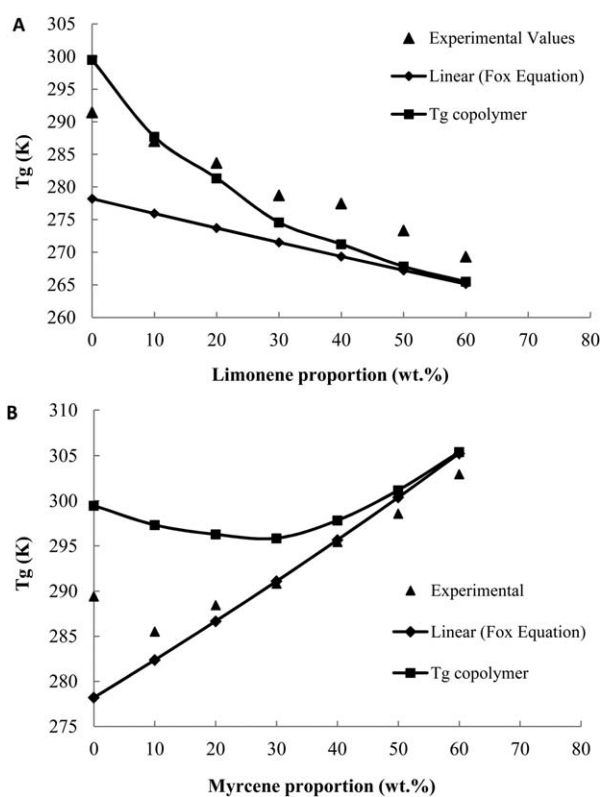
the experimental conditions, both structures are likely to be formed (the linear molecules and the cross-linked structure) and the generation of this reticulated Polymyrcene network is responsible for the increase in the glass transition temperature observed in the experimental results. The divergence between the experimental data and the values predicted by the model could be associated to the fact that triglyceride-based polymers are very complex materials, containing cross-linker molecules with a range of functionalities.

CONCLUSIONS

Thermosets were prepared through copolymerization of TO with Lim, Myr, and styrene. The Tg was found to be a function of both the type and comonomer weight content. Young's modulus and the experimental cross-linking densities decreased as comonomer weight content increased. The Fox and Loshaek model showed a relatively good prediction of the Tg values for TO–Lim copolymers. For Myr, Tg values matched those predicted by the Fox equation. Even though triglyceride-based polymers are complex materials, some of the thermo-mechanical properties were found to be predictable by simple mathematical approaches and models developed for polyvinyl resins.

ACKNOWLEDGMENTS

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